Supporting Information for:

Catalysis of Proton Reduction by a $[BO_4]$-bridged Dicobalt Glyoxime

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Experimental Details

All solvents were of commercial grade and dried over activated alumina using a Grubbs-type solvent purification system prior to use. All chemicals were from major commercial suppliers and used as received without further purification. ^{1}H and ^{13}C NMR spectra were collected on 300, 400, or 500 MHz Varian spectrometers and referenced to the residual protio-solvent signal[1] in the case of ^{1}H and ^{13}C or the deuterium lock signal in the case of ^{11}B. Chemical shifts (δ) are reported in units of ppm and coupling constants (*J*) are reported in Hz. Mass spectra were obtained with a PE SCIEX API 365 triple quadrupole spectrometer.

Protonated dimethylformamide ($[DMFH]^{+}OTf^{-}$) was synthesized according to the method of Favier and Duñach.[2] $Co^{III}(dmgH)_2(MeCN)Cl$ was synthesized according to the published method.[3] $Co^{III}(dmgBF_2)_2(MeCN)Cl$ was synthesized according to the published method.[4]

Caution! Trimethyl borate is moisture sensitive and should be handled under inert atmosphere.

$[BO_4]$-bridged dicobalt glyoxime (3)

A three-neck 500-mL round-bottom flask containing **1** (1.0 g, 3.08 mmol) was fitted with a condenser, evacuated, and refilled with N_2(g). MeCN (250 mL) was cannula transferred into the flask, and trimethyl borate (1.72 mL, 15.4 mmol) was then syringed into the solution. The mixture immediately changed from green to brown. Tetraethylammonium chloride (255 mg, 1.54 mmol) was then added to the solution. After refluxing for 3 h, the solution was cooled to room temperature and reduced in volume to ~50 mL. The addition of diethyl ether resulted in precipitation of a silvery, gray solid that was isolated by filtration. Upon drying, the solid turns brown. The brown solid was washed with dicholoromethane, yielding a darker brown solid that can be recrystallized with MeCN/diethyl ether. Yield: 937 mg, 1.1 mmol, 70%. ^{1}H NMR (400 MHz, MeCN-d_3) δ 18.39 (s, 2H), 3.17 (q, J = 7.3 Hz, 8H), 2.56 (s, 12H), 2.47 (s, 12H), 1.22 (t, J = 7.2 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (101 MHz, MeCN-d_3) δ 160.7, 150.1, 52.1, 13.7, 12.3, 6.7. ^{11}B NMR (128 MHz, MeCN-d_3) δ 7.41. ESI-MS (negative) m/z: found 727.1 m/z (**3** – NEt_4), 693.1 (**3** – NEt_4 – Cl^{-} – H^{+}), 657.0 (**3** – NEt_4 – $2Cl^{-}$ – $2H^{+}$), 621.0 (**3** – NEt_4 – $3Cl^{-}$ – $3H^{+}$).

Regarding the synthesis of dimer **3**, we note that higher oligomers were not observed or isolated under the conditions used here despite the presence of excess trimethyl borate. We propose that the dimeric structure is relatively stable, considering the high yield obtained. Oligomeric complexes would presumably have higher negative charges (–1 per monomer) perhaps minimizing their formation by reduced stability.

X-ray crystallography

Single-crystal diffraction data were collected with a Bruker KAPPA APEXII X-ray diffractometer. CCDC entry 1013942 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

Electrochemistry

Electrochemistry was performed in a nitrogen-filled glove box with 0.10 M tetra(n-butylammonium) hexafluorophosphate (n-Bu_4NPF_6, Fluka electrochemical grade) in acetonitrile as the supporting electrolyte. Measurements were made with a Gamry Reference 600 potentiostat/galvanostat using a standard three-electrode configuration.

The working electrode was the basal plane of highly oriented pyrolytic graphite (HOPG) (GraphiteStore.com, Buffalo Grove, Ill.; surface area: 0.09 cm^2), the counter electrode was a platinum wire, and a silver wire immersed in electrolyte served as a pseudo-reference electrode. The reference was separated from the working solution by a Vycor frit (Bioanalytical Systems, Inc.)

Ferrocene (Strem Chemicals, 99%) was added to the electrolyte solution at the conclusion of each experiment (~1 mM); the midpoint potential of the ferrocenium/ferrocene couple (denoted as $Fc^{+/0}$) served as an external standard for comparison of the recorded potentials.

Concentrations of analyte for cyclic voltammetry were typically 0.5 mM.

Controlled-potential electrolysis coupled to product detection was carried out with a standard three-electrode configuration in a custom two-compartment air-tight cell. The working electrode consisted of a ca. 10 cm^2 block of HOPG. The reference and counter electrodes were as described above. The volume of solution held by the cell in total was 70 mL, with ca. 100 mL of total headspace volume.

For the bulk generation of hydrogen by electrolysis at –1.5 V, the concentration of dimer **3** was 0.5 mM and the concentration of buffered acid (1:1 $[DMFH]^+$:DMF) was 5 mM. Consistent with cyclic voltammetry as well as literature results,[5] some background current for hydrogen production was observed. However, this current was far below that measured for catalysis with **3**.

Homogeneity of catalysis with **3** was studied by checking the electrode surface for formation of Co particles following catalysis, as has been observed with some other glyoxime-type complexes under organic[6] and aqueous[7] conditions. Specifically, an electrode used for extensive catalysis with **3** was compared to a fresh, clean electrode by voltammetry in the presence of acid. We found the response of a clean carbon electrode in the presence of 10 mM 1:1 $[DMFH]^+$:DMF to be virtually identical to a carbon electrode previously used for extensive catalysis experiments. Additionally, cyclic voltammograms of solutions containing **3** and excess acid were virtually identical before and after extensive electrolysis.

Gas chromatography

Gas analysis for the controlled-potential electrolyses was performed with an Agilent 7890A gas chromatograph with separate columns for analysis of hydrogen gas and nitrogen, oxygen, carbon dioxide, carbon monoxide, hydrogen disulfide, methane, ethane, ethylene, and ethyne. The instrument was calibrated with a standard gas mixture to obtain quantitative data.

The air-tight electrochemical cell was prepared in a nitrogen-filled glovebox. A background experiment before electrolysis confirmed only nitrogen and minimal oxygen in the glovebox atmosphere. Following 1.25 hr of electrolysis, headspace gas was analyzed for dihydrogen content. No other reduction products were detected.

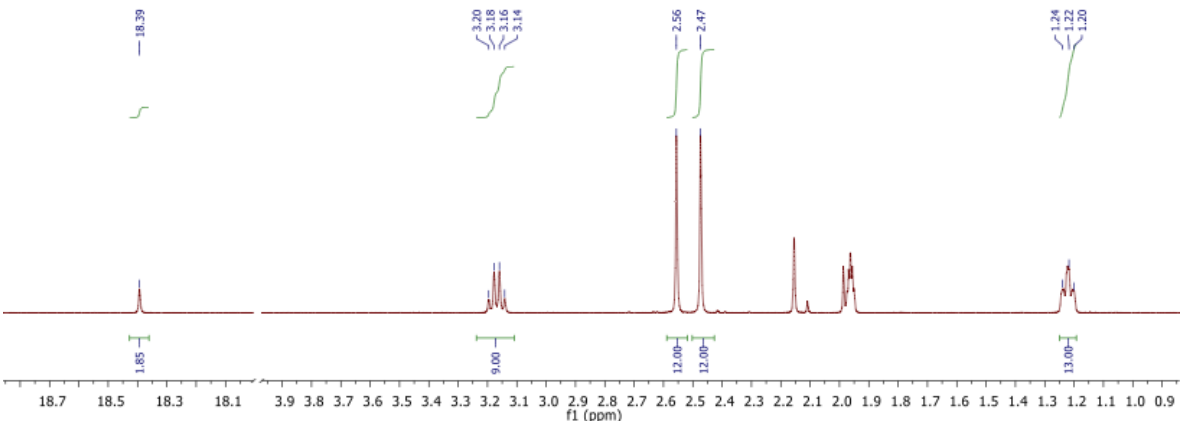

Figure S1. ^{1}H NMR spectrum of **3** in CD_3CN.

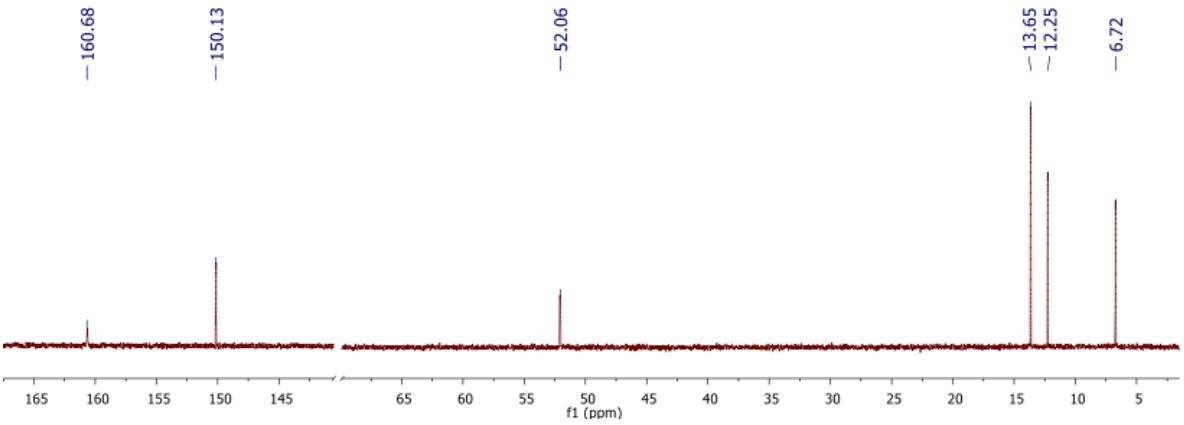

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in CD_3CN.

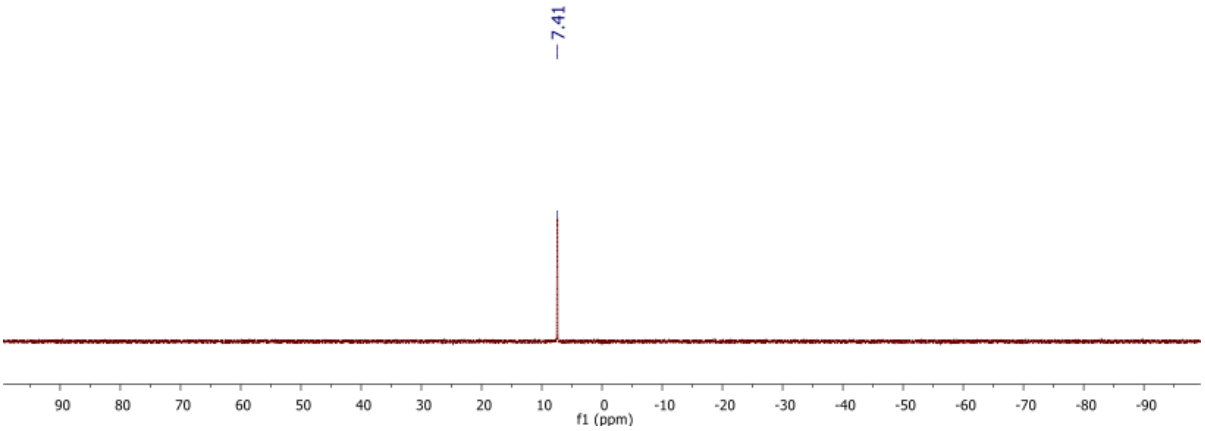

Figure S3. ^{11}B NMR spectrum of **3** in CD_3CN.

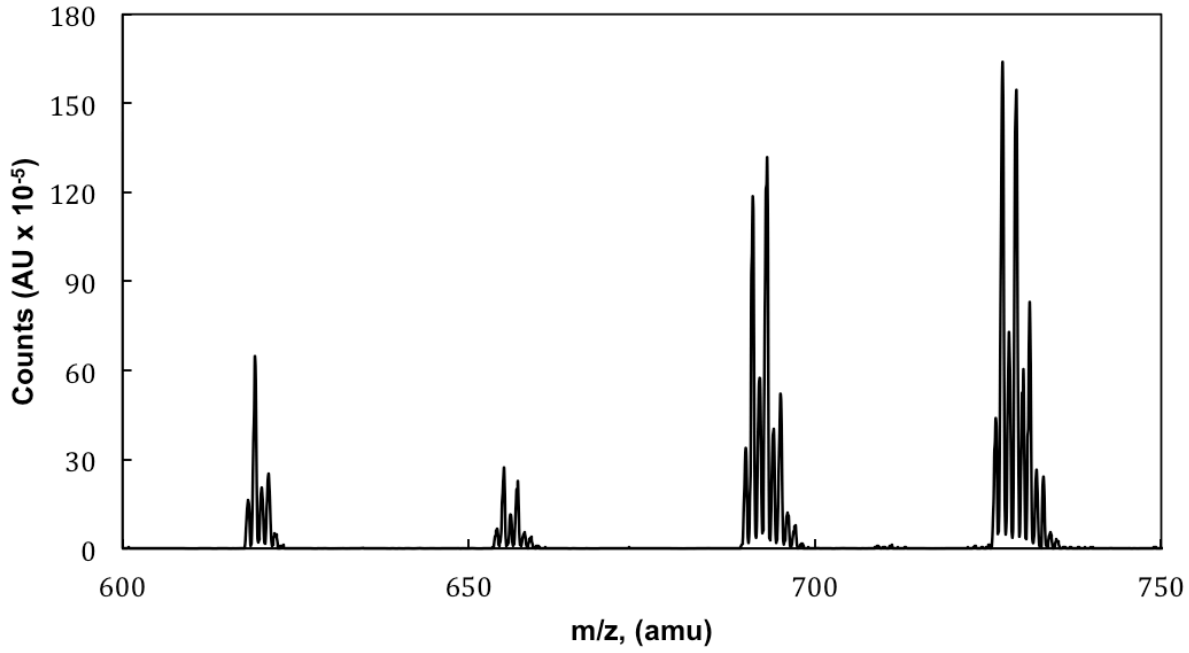

Figure S4. Mass spectrum of **3** in the negative-ion mode.

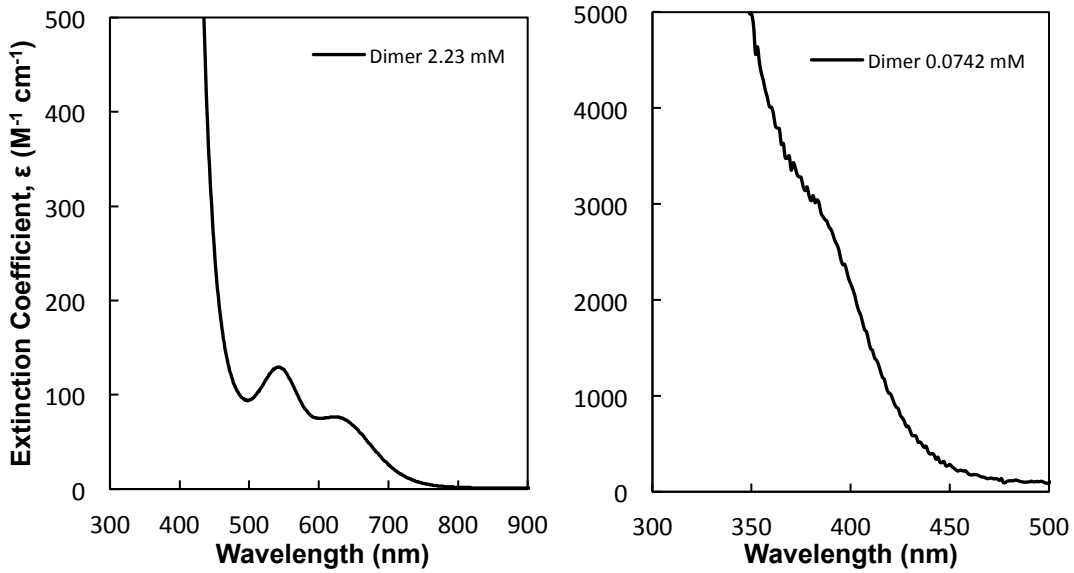

Figure S5. UV-visible absorption spectra of the BO_4^--bridged dimeric cobaloxime at 2.23 mM (left) and 0.0742 mM (right).

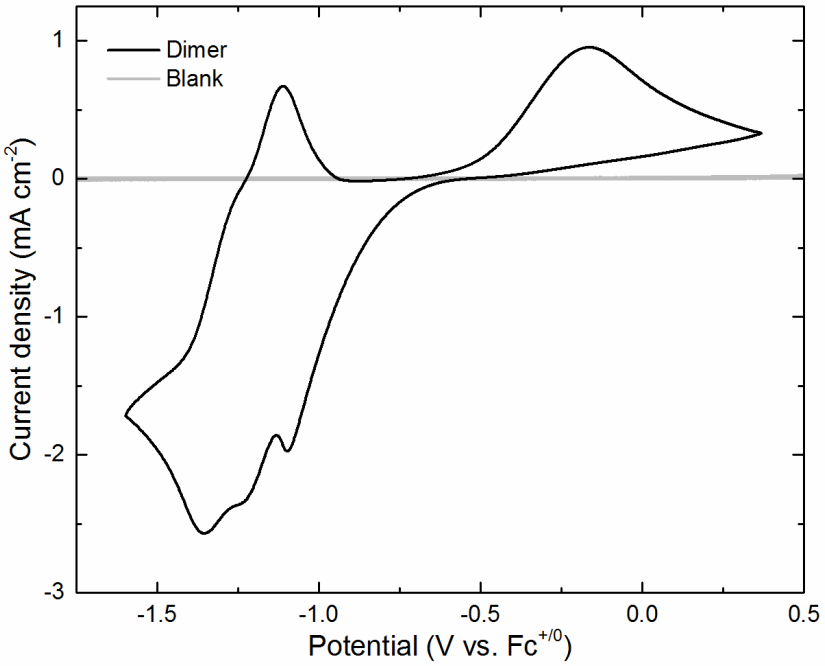

Figure S6. Full cyclic voltammogram of **3**. An irreversible oxidation was observed at approximately –0.15 V vs $Fc^{+/0}$ and is assigned to oxidation of Co(III) to Co(II). Near –1 V, reduction of Co(III) to Co(II) was observed. At more negative potentials, two closely spaced couples were observed near –1.2 and –1.3 V vs $Fc^{+/0}$ and these are assigned to single-electron $Co^{II/I}$ couples (see main text).

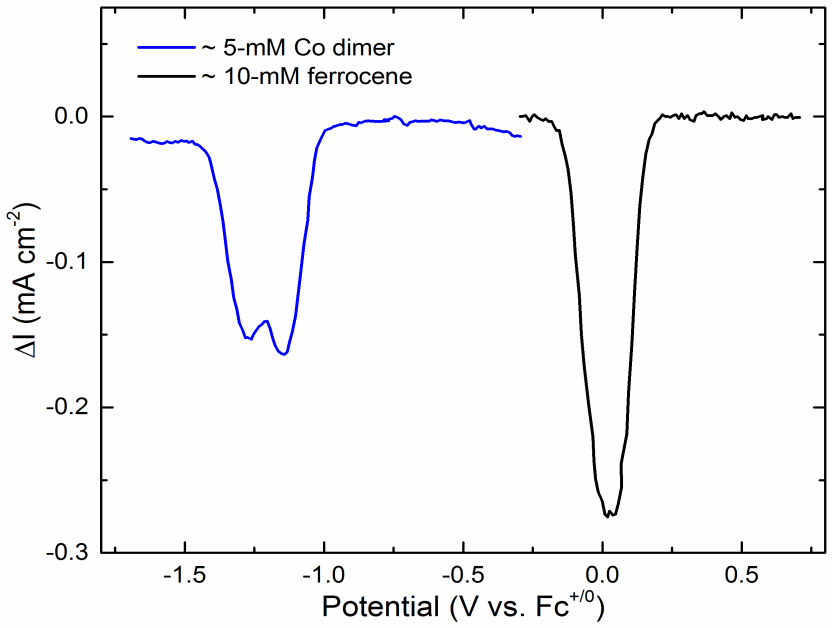

Figure S7. To better establish the number of electrons participating in the oxidation and reduction of **3**, differential pulse voltammetry was carried out using the same electrode configuration as above (Figure S6). Two closely spaced, but resolved, signals were observed on an oxidative sweep for a sample of 5 mM of the dimer in a NBu_4PF_6 acetonitrile solution, implying that two unique processes were occurring. A reductive sweep on a 10 mM solution of ferrocenium produced a clean single peak with an area roughly equal to that of the two peak areas for **3**. The 1:1 comparison implies that indeed there is an overall two-electron process occurring as the two metal centers in the complex are oxidized from Co^{I} to Co^{II}.

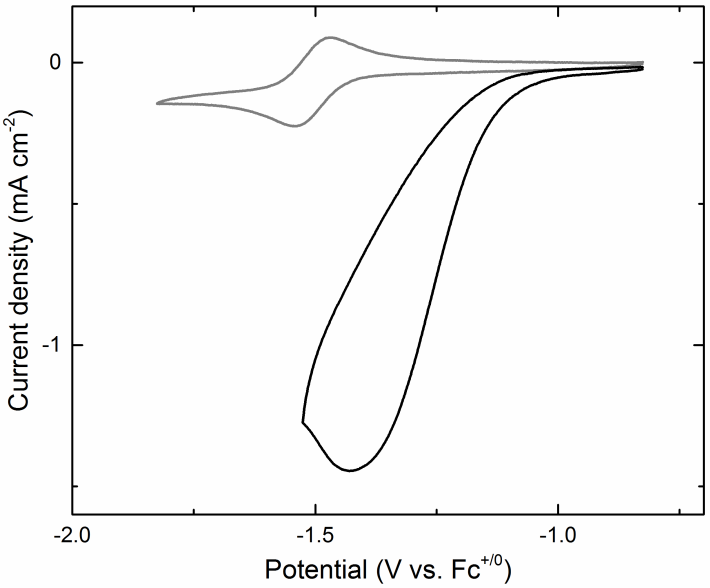

Figure S8. Cyclic voltammetry of **1** with 5 mM 1:1 mixture of $[DMFH]^+$ and DMF (black line) and reversible response in the absence of acid (gray line)

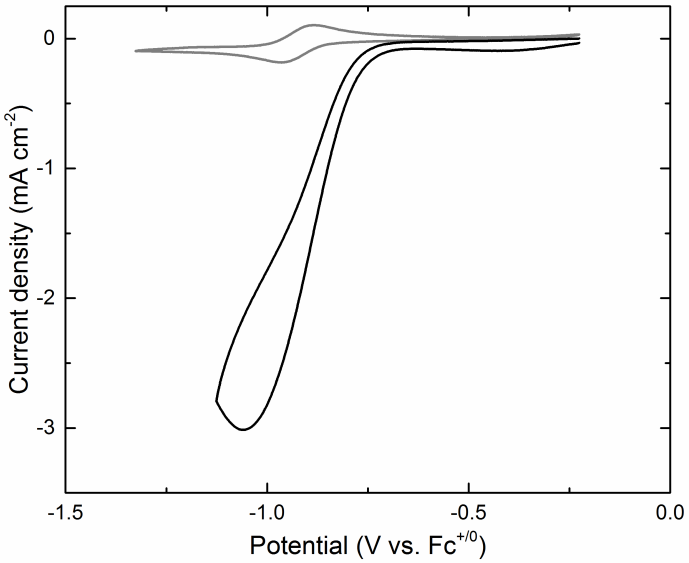

Figure S9. Cyclic voltammetry of **2** with 5 mM 1:1 mixture of $[DMFH]^+$ and DMF (black line) and reversible response in the absence of acid (gray line).

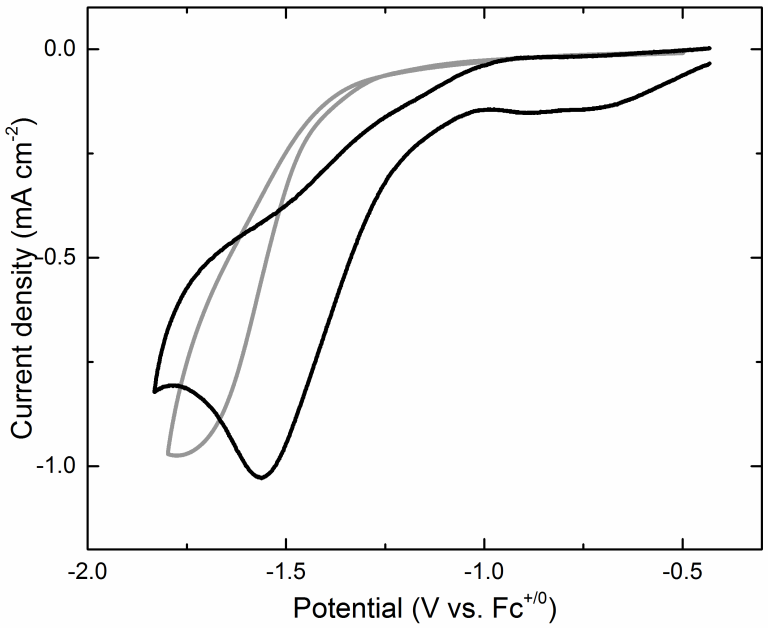

Figure S10. Comparison of the cyclic voltammetric response of **3** in the presence of 5 mM 1:1 $[DMFH]^+$:DMF (black line), and the response of the bare electrode only with 5 mM acid (gray line).

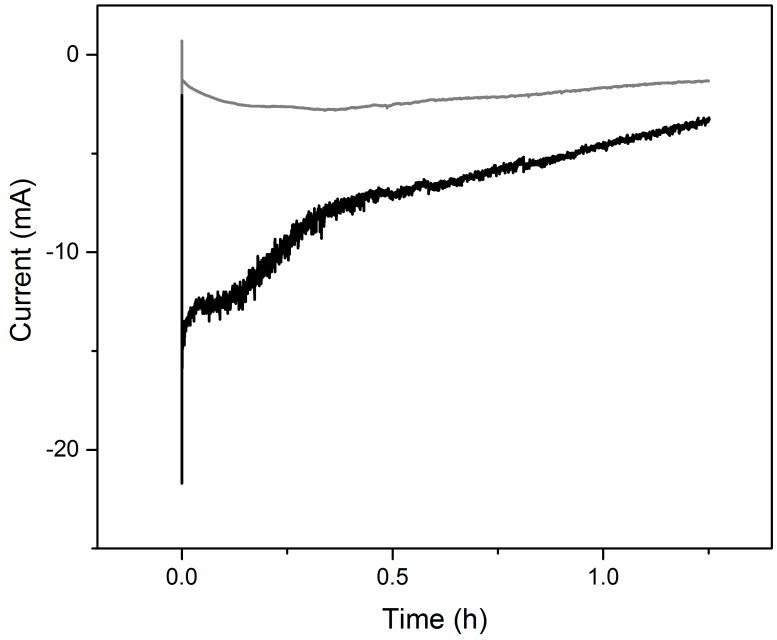

Figure S11. Comparison of steady-state currents flowing during electrolysis at -1.5 V. Response in the presence of dimer **3** and 5 mM 1:1 $[DMFH]^+$:DMF (black line) and in the presence of only 5 mM 1:1 $[DMFH]^+$:DMF (gray line).

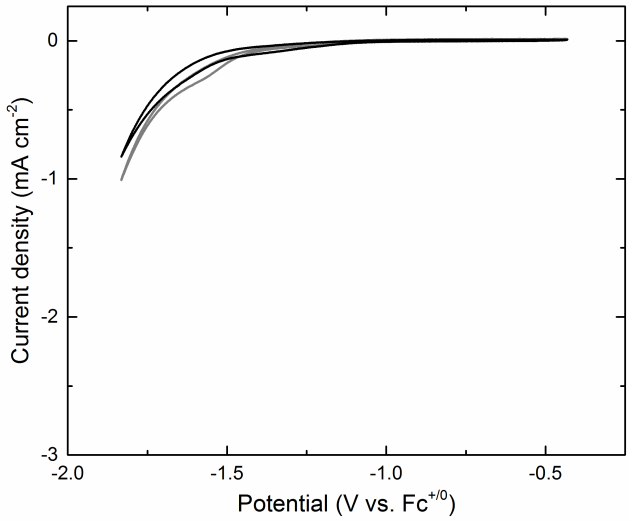

Figure S12. A test for formation of Co particles on the electrode surface was carried out by comparison of cyclic voltammetry with acid before and after running catalytic experiments with dimer **3**. Specifically, the response of a clean carbon electrode in the presence of 10 mM 1:1 $[DMFH]^+$:DMF (gray line) was virtually identical to a carbon electrode previously used for extensive catalysis experiments with **3** (black line).

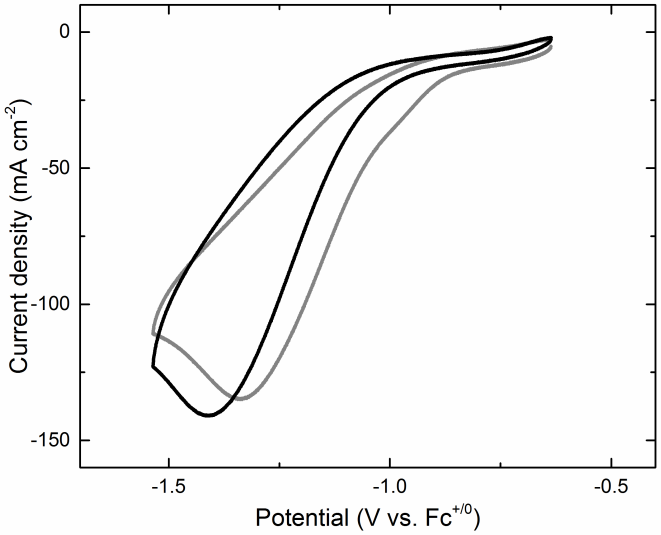

Figure S13. A test of the stability of **3** under electrocatalytic conditions was carried out by collecting a cyclic voltammogram of **3** (~0.5 mM) in the presence of excess 1:1 $[DMFH]^+$:DMF (~10^{-3} M) before (gray line) and after (black line) electrolysis of the solution at –1.5 V for 1 h. Only minor differences were apparent, suggesting that **3** is stable under electrocatalytic conditions.

X-ray Structural Data

Table S1. Crystal data and structure refinement for the cobalt dimer **3**.

Chemical formula	$C_{26}\,H_{49}\,B\,Cl_4\,Co_2\,N_{10}\,O_8$
Formula weight	900.22
Crystallization solvent	Acetonitrile, diethyl ether
Crystal habit	Blade
Crystal size	0.59 x 0.27 x 0.07 mm^3
Crystal color	Brown
Data collection	
Type of diffractometer	Bruker KAPPA APEXII
Wavelength	0.71073
Data collection temperature	100(2) K
Crystal system	Triclinic
Space group	P -1
Cell dimensions	
	a = 12.5189(7) Å α = 109.121(2) °
	b = 12.7064(7) Å β = 102.053(2) °
	c = 13.0978(8) Å γ = 90.025(2) °
Cell volume	1919.77(19)
Z	2
Density (calculated)	1.557 Mg/m^3
F(000)	932
q range for data collection	1.668 to 43.747 °
Index ranges	-24≤h≤24 -24≤k≤24 -25≤l≤25
Data collection scan type	f and ω scans
Reflections collected	288113
Absorption coefficient	1.201
Max. and min. transmission	0.921 and 0.538
Refinement	
Structure solution program	XT-2014/1 (Sheldrick, 2012)
Structure refinement program	SHELXL-2014/2 (Sheldrick, 2014)
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	29359 / 0 / 662
Goodness of fit	1.284
Final R indices[I > 2\s(I), 29359 reflections]	R1 = 0.0317, *w*R2 = 0.0716
R indices (all data)	R1 = 0.0533, *w*R2 = 0.0771
Weighting scheme	Calc $w=1/[\sigma^2Fo^2+(0.0300P)^2]$ $P=(Fo^2+2Fc^2)/3$
Max shift/error	0.004
Average shift/error	0.000
Largest diff. peak and hole	0.877 and -0.662 $Å^3$

Table S2. Selected lengths (Å) and angles (°) for the cobalt dimer **3**.

Co(1)-Co(2)	6.316(2)	Co(2)-N(8)-C(14)	116.50(5)
Co(1)-Cl(1)	2.2314(4)	Cl(1)-Co(1)-Cl(2)	176.42(2)
Co(1)-Cl(2)	2.2343(4)	Cl(1)-Co(1)-N(1)	89.44(2)
Co(1)-N(1)	1.8867(7)	Cl(1)-Co(1)-N(2)	89.42(2)
Co(1)-N(2)	1.8856(6)	Cl(1)-Co(1)-N(3)	88.36(2)
Co(1)-N(3)	1.8903(6)	Cl(1)-Co(1)-N(4)	90.67(2)
Co(1)-N(4)	1.8831(7)	Cl(2)-Co(1)-N(1)	88.24(2)
Co(2)-Cl(1)	2.2258(3)	Cl(2)-Co(1)-N(2)	92.93(2)
Co(2)-Cl(2)	2.2352(3)	Cl(2)-Co(1)-N(3)	89.32(2)
Co(2)-N(1)	1.8770(7)	Cl(2)-Co(1)-N(4)	91.70(2)
Co(2)-N(2)	1.8878(7)	N(1)-Co(1)-N(2)	81.62(3)
Co(2)-N(3)	1.8832(7)	N(1)-Co(1)-N(3)	98.89(3)
Co(2)-N(4)	1.8829(8)	N(1)-Co(1)-N(4)	178.94(3)
O(1)-N(1)	1.3343(8)	N(2)-Co(1)-N(3)	177.72(3)
O(2)-N(2)	1.3673(7)	N(2)-Co(1)-N(4)	97.32(3)
O(3)-N(3)	1.3264(8)	N(3)-Co(1)-N(4)	82.17(3)
O(4)-N(4)	1.3662(7)	Cl(3)-Co(2)-Cl(4)	178.15(2)
O(5)-N(4)	1.3648(8)	Cl(3)-Co(2)-N(5)	92.64(2)
O(6)-N(6)	1.327(1)	Cl(3)-Co(2)-N(6)	88.53(2)
O(7)-N(7)	1.3629(9)	Cl(3)-Co(2)-N(7)	93.27(2)
O(8)-N(8)	1.3384(9)	Cl(3)-Co(2)-N(8)	88.92(2)
B(1)-O(2)	1.470(1)	Cl(4)-Co(2)-N(5)	88.32(2)
B(1)-O(4)	1.4870(8)	Cl(4)-Co(2)-N(6)	90.04(2)
B(1)-O(5)	1.4747(8)	Cl(4)-Co(2)-N(7)	88.16(2)
B(1)-O(7)	1.477(1)	Cl(4)-Co(2)-N(8)	90.14(2)
		N(5)-Co(2)-N(6)	82.15(3)
Co(1)-B(1)-Co(2)	145.21(1)	N(5)-Co(2)-N(7)	97.48(3)
Co(1)-N(1)-O(1)	122.00(5)	N(5)-Co(2)-N(8)	178.31(3)
Co(1)-N(2)-O(2)	124.51(5)	N(6)-Co(2)-N(7)	178.17(3)
Co(1)-N(3)-O(3)	122.06(5)	N(6)-Co(2)-N(8)	98.55(3)
Co(1)-N(4)-O(4)	125.11(5)	N(7)-Co(2)-N(8)	81.78(3)
Co(2)-N(5)-O(5)	125.04(4)	N(2)-O(2)-B(1)	117.22(5)
Co(2)-N(6)-O(6)	122.34(5)	N(4)-O(4)-B(1)	118.64(5)
Co(2)-N(7)-O(7)	124.43(5)	N(5)-O(5)-B(1)	117.89(5)
Co(2)-N(8)-O(8)	122.22(5)	N(7)-O(7)-B(1)	118.08(5)
Co(1)-N(1)-C(1)	116.46(5)	O(2)-B(1)-O(4)	117.76(6)
Co(1)-N(2)-C(2)	116.83(5)	O(2)-B(1)-O(5)	100.01(5)
Co(1)-N(3)-C(5)	115.80(5)	O(2)-B(1)-O(7)	104.22(5)
Co(1)-N(4)-C(6)	116.15(5)	O(4)-B(1)-O(5)	104.07(5)
Co(2)-N(5)-C(9)	116.39(5)	O(4)-B(1)-O(7)	113.11(6)
Co(2)-N(6)-C(10)	115.86(5)	O(5)-B(1)-O(7)	117.54(6)
Co(2)-N(7)-C(13)	116.34(5)	O(1)-N(1)-C(1)	121.53(7)

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